Technical, economic and environmental evaluation of advanced tertiary treatments for micropollutants removal (oxidation and adsorption)

S. Besnault, S. Martin Ruel, S. Baig, M. Esperanza, H. Budzinski, Cecile Miege, C. Boucher, K. Le Menach, Marina Coquery

(P29) Technical, economic and environmental evaluation of advanced tertiary treatments for micropollutants removal (oxidation and adsorption)

S. Besnault *, S. Martin Ruel *, S. Baig, M. Esperanza*, H. Budzinski***, C. Miege****, C. Boucher**, K. Le Menach*** and M. Coquery******

* CIRSEE, Suez Environnement, 38 rue du Président Wilson, 78230 Le Pecq, France (E-mail: *Sophie.Besnault@suez-env.com*)

** Degrémont SAS, 138 avenue du 18 juin 1940, 92500 Rueil Malmaison, France

*** Université Bordeaux 1, CNRS, EPOC/LPTC UMR5805, 351 Cours de la libération 33405 Talence cedex, France

**** Irstea, UR MALY (Freshwater Systems, Ecology and Pollution research unit), 5 rue de la Doua, CS70077, 69626 Villeurbanne Cedex, France

Abstract

Two pilots for tertiary treatment, an advanced oxidation processes (AOP - O_3/UV/H_2O_2) pilot and a granular activated carbon pilot, were tested in three different wastewater treatment plants after a secondary treatment. A total of 64 micropollutants including drugs, pesticides, alkylphenols, PAHs and metals were analysed in the samples at the inlet and the outlet of the pilots. The tertiary treatments studied (ozone, AOP and activated carbon) were efficient for the removal of most of the compounds analysed in this study, except metals. The addition of hydrogen peroxide to ozone increased the number of substances well removed but it did not improve the removal of substances that readily react with ozone (such as betablockers or carbamazepine). The other AOP (ozone/H_2O_2 and UV/H_2O_2) did not improve the number of substances well removed in comparison with ozone alone. The granular activated carbon was still efficient (R>70%) after 6 months working 24/7 for most of the drugs and the urea and triazine pesticides. The 5 technologies studied were sized at full scale in order to calculate their cost for two sizes of WWTP. The implementation of a tertiary treatment on a 60 000 to 200 000 PE WWTP would increase the wastewater treatment cost by 1,5 to 17,6 euros cents per cubic meter treated according to the technology and the removal objective. Concerning the environmental impact, for the big WWTP, the activated carbon is more impacting than the other processes for most of the impacts calculated. The order of POA by increasing environmental impact is ozone < ozone/H_2O_2 < ozone/UV ~ UV/H_2O_2. For the medium size WWTP however, the activated carbon is comparable to the other solutions regarding environmental impact.

Keywords

Ozone; Advanced Oxidation Processes; Granular Activated Carbon; Micropollutants removal; Cost; Environmental impact

INTRODUCTION

One of the next major challenges of wastewater treatment is to reliably remove micropollutants and the related toxicity from treated water. Although they were not initially designed for this purpose, conventional wastewater treatment plants (WWTP) can eliminate part of the micropollutants by adsorption on sludge, biodegradation and/or volatilisation (Choubert *et al*., 2010). However, some micropollutants remain in treated wastewater. Tertiary treatments can be implemented to help reaching concentration values compatible with a good status of the receiving water bodies.

This study was focused on two types of tertiary treatment investigated at pilot scale in three wastewater treatment plants. A pilot plant consisting in advanced oxidation processes (AOP) combining ozone, UV and hydrogen peroxide (Meier *et al.*, 2011) was tested in two plants with different upstream treatment processes: plant A, a membrane bioreactor; and plant B, a low load activated sludge followed by a sand filter. A granular activated carbon (GAC) filtration pilot was operated in plant C, a low load activated sludge followed by a sand filter and ozone for disinfection.

The objectives of the study were to evaluate and compare the performance of oxidation and adsorption for micropollutants removal, to assess the costs of these processes and their environmental impact.

MATERIAL AND METHODS

A total of 64 micropollutants were analysed in the samples of this study with several analytical techniques based on mass spectrometry. The selected substances and the analytical techniques are presented in table 1.

Table 1. Micropollutants analysed in this study and quantification methods.

Family of substances	Substances	Preparation/ Extraction	Analytical techniques	Limits of quantification (ng/L)
Betablockers (4)	Atenolol, metoprolol, propranolol, sotalol	SPE	HPLC/MS/MS	0.5 to 1
Antibiotics (10)	Sulfamethazine, sulfadimethazine, sulfamethoxazole, sulfadiazine, trimethoprim, erythromycin, roxithromycin, clindamycin, lincomycin, tylosin	SPE	HPLC/MS/MS	5 to 280
Other drugs (4)	Carbamazepine, diazepam, ibuprofen, diclofenac	SPE	HPLC/MS/MS	0.5 to 1
Herbicides, pesticides (2)	Glyphosate, AMPA	Derivation	HPLC/MS/MS	100
Herbicides, pesticides (4)	Atrazine, simazine, diuron, isoproturon	SPE	HPLC/MS/MS	5 to 15
Alkylphenols (6)	4-nonylphenol monoethoxylate, 4-nonylphenol diethoxylate, 4-nonylphenol, 4-ter octylphenol, 4-nonylphenoxyacetic acid, 4 ter butylphenol	SPE or SPME	LC/MS/MS and GC/MS	1 to 10
Polycyclic Aromatic Hydrocarbons (19)	Napthalene, dibenzothiophene, phenanthrene, anthracene, acenaphthylene, acenaphtene, fluorene, fluoranthene, pyrene, benzo(a)anthracene, chrysene + triphenylene, 2,1 benzo-naphtothiophene, benzo(b+j+k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(c-d)pyrene, dibenzo(a,h + a,c)anthracene, benzo(ghi)perylene	SPME	GC/MS	0.1 to 1
Metals (15)	B, Ti, V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Sn, Ba, Pb, U	-	ICP-MS	10 to 2000

MAJOR RESULTS AND CONCLUSIONS

Technical evaluation

Over 70% removal was obtained for 70% of the organic micropollutants studied by implementing ozone in optimized conditions (3 minutes contact time) and ozone dose (5 gO_3/m^3 ozone dose applied). Figure 1 displays the best results obtained according to the oxidation system.

Improvements resulting from AOPs concern:

- Compounds less reactive towards ozone: an addition of H_2O_2 to ozone increased the removal yield of pesticides by 5 to 50 %;
- Accordingly, removal yields of specific compounds were increased depending on operating conditions. For example, pesticides were better removed with the O_3/H_2O_2 solution with an excess of H_2O_2;
- Only the O_3/H_2O_2 system increased significantly the number of substances well removed (> 70%) in comparison with ozonation alone versus UV-AOPs.

However, the improvement's extend may both depend on the conditions for AOP application and on the compound nature (aromatic rings, high electronic density functions...).

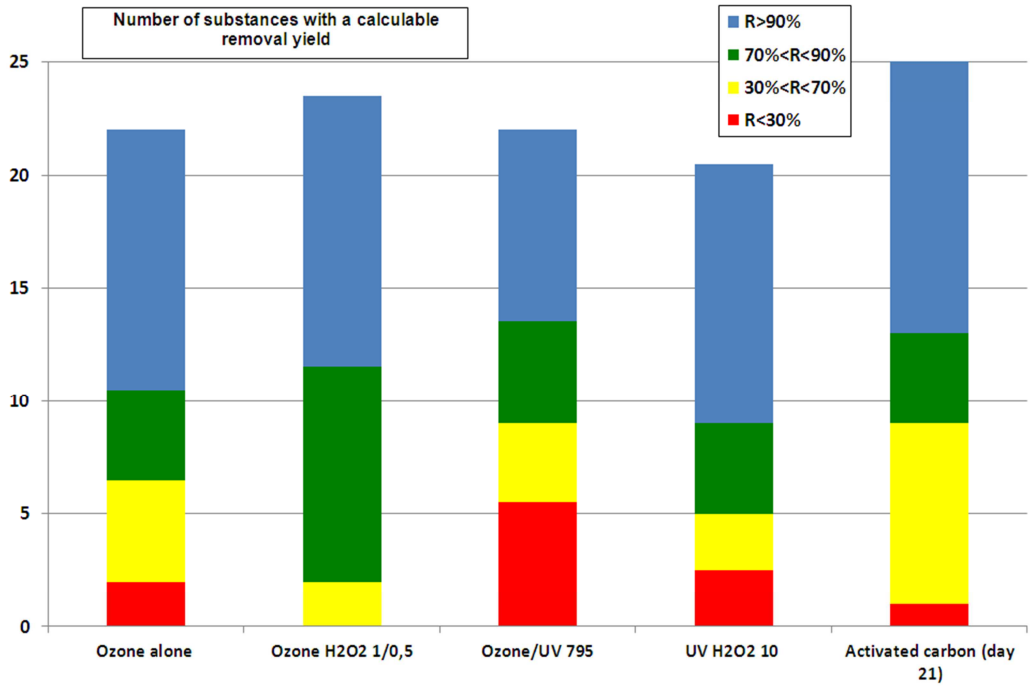

Figure 1. Number of organic substances with a calculable removal yield by categories for each of the advanced tertiary treatments applied in this study (under 30% red, between 30 and 70% yellow, between 70% and 90% green and over 90% blue).

The application of GAC filtration subsequent to ozone disinfection achieved high removal yields for drugs and pesticides, except glyphosate and AMPA. It is worth noting that the activated carbon treatment was still efficient for the removal of these molecules after 6 month operation. Some metals were also adsorbed by the activated carbon in particular at the beginning of the test (B, Cr, Zn, Pb) but the removal yield decreased over time. About 65% of the organic micropollutants studied were removed over 70% by GAC after 3 weeks functioning 24/7 (Figure 1). Removal yields of some of the organic compounds then decreased over time.

Economic evaluation

The investments and operations costs (CAPEX and OPEX) of the tertiary treatments studied were evaluated by extrapolating the results of the pilot trials to two hypothetical full scale wastewater treatment plants: a 200 000 PE WWTP and a 60 000 PE WWTP. The design of the full scale tertiary treatment was done considering an objective of at least 70% removal for 75% of the organic micropollutants analysed in this study.

As expected, treating the micropollutants may represent a significant specific additional cost:

- In proportion higher for a low/medium capacity of the plant than for a high capacity plant;
- Highly dependent on the technology;
- Additional treatment cost of 1.5 to 17.6 € cents per treated cubic meter of wastewater, corresponding to a bill of 1.3 to 16 € per inhabitant per year.

Environmental evaluation

The environmental impact of the tertiary treatment was assessed according to a Life Cycle Analysis methodology based on the operation of full scale treatments as defined in the economic study, allowing a comparison of the different technologies. However, the environmental impact evaluation is not a Life Cycle Analysis as only the operation phase was taken into account and not the construction phase.

For the 200 000 PE WWTP, the activated carbon is more impacting than the other processes for most of the impacts calculated (Figure 2), in particular for the impacts concerning land occupation, due to the activated carbon's end of life (in landfill in this study). The order of POA by increasing environmental impact is ozone < ozone/H_2O_2 < ozone/UV ~ UV/H_2O_2.

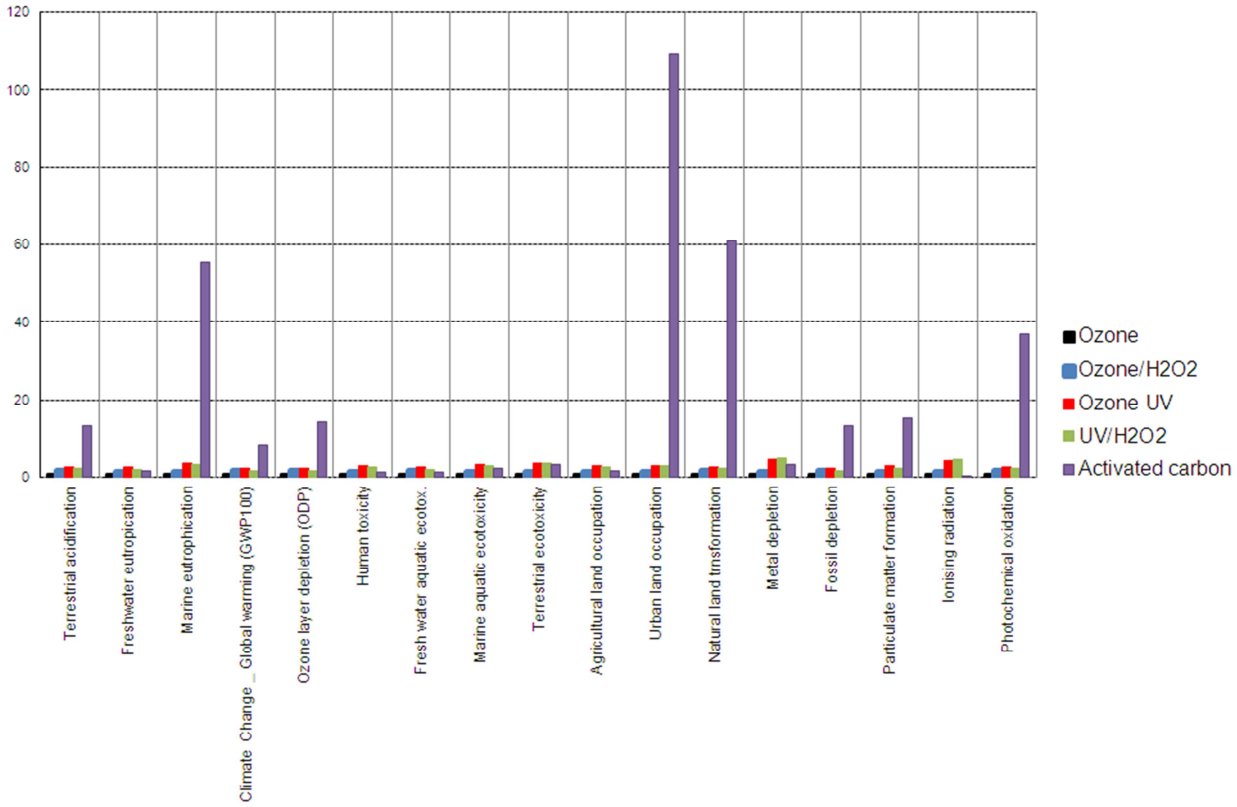

Figure 2. Normalised environmental impacts for the 200 000 PE WWTP

For 60 000 PE WWTP however, the activated carbon is comparable to the other solutions regarding environmental impact. The activated carbon is less impacting than AOPs concerning some impacts (ionising radiation, fresh water eutrophication and human toxicity) but it is more impacting for fossil depletion, particulate matter formation and land occupation impacts.

REFERENCES

Choubert J.-M., Martin-Ruel S., Esperanza M., Budzinski H., Miege C., Lagarrigue C., Coquery M. 2010 Limiting the emissions of micro-pollutants what efficiency can we expect from wastewater treatment plants ? *Water Science and Technology*, **63**(1), 57-65.

Meier D., Uttinger W., Baig S., Romancuk M. Bressmer S., Krogh F. & Paolini B. 2011 Design and performance of a mobile pilot plant for the evaluation of AOP in waste water treatment, *IOA IUVA World congress and exhibition-Proceedings*, I.6.10, 1-6